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titled

"Search for Biological Precursor Molecules  
in Volcanic Volatile Systems"

Prepared by

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1. Subject: Annual Status Report  
NASA Grant NGR-12-001-012
2. Title: "Search for Biological Precursor Molecules in  
Volcanic Volatile Systems."

3. Abstract.

23603

The research consists of the following two parts - (1) an investigation of the natural volcanic gaseous system for its elemental and molecular composition, with particular emphasis on compounds of biological importance which might be present in trace quantities. (2) A field or laboratory investigation of the equilibrium molecular and free radical components to be found in gaseous systems which contain the major elements (O, H, C, S, N) of volcanic gas. This last is pertinent since we have found from work on Hawaiian volcanoes that the gases are a homogenous system in thermodynamic equilibrium. Investigations of pockets or vesicles of gas in newly erupted lavas, and of similar gaseous or fluid inclusions in ultrabasic nodules found in lava, which seem to have a deep-seated source, also are being made with the search for prebiotic components as the objective.

*Auth*

4. General Statement.

This grant was activated on February 1, 1965, but due to certain delays it did not become operative for experimental work until mid-March. Much of the effort has been devoted to equipment construction and sample collection, but a few

tentative preliminary results have been obtained.

For the volcanic gas collection phase, in work of this character depending on the unpredictable conditions at erupting vents, the investigations are very much "researches-of-opportunity." Since 1960 they have been patterned by the occurrence of three flank eruptions of Kilauea (Kilauea Iki 1959-60, Alae - 1963, and Makaopuhi - 1965) which partly filled old pit craters with molten lava lakes. The lakes quickly crusted over, but have molten lava cores which will continue to solidify for some years (Kilauea Iki and Makaopuhi--Alae has solidified completely). These lakes have given us an unprecedented opportunity for studies of the geology, mineralogy, physics and chemistry of large molten rock bodies and the solidification processes in such systems. In our recent researches on volcanic gas, we have concentrated on collections and measurements made to follow the degassing process at these unique sites.

The researches on which all recent work is based were carried out during the 1959-1960 eruption of Kilauea at Kilauea Iki. At that time gas samples were taken also from quiet vents and degassing pumice mounds. A new technique, based on the separation of reactive gases in the collecting tubes by adsorption on silica gel, was used in the collection of samples. The samples were analyzed by gas chromatography and were found to be principally  $H_2O$  and  $CO_2$ , with lesser

amounts of  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{CO}$  and  $\text{CH}_4$ . Complex equilibrium calculations were carried out on an IBM 650 computer, using a general method of minimizing the free energy. A study was made of the equilibrium variation of a typical volcanic gas phase with temperature, pressure, oxidation state and water content. A graphical method, similar to logarithmic-pH diagrams, was developed to systematize the variation of a volcanic gas with oxidation state. Comparison of the analyses of samples collected at Kilauea Iki and Kapoho with the calculated equilibrium composition at the temperature of collection indicated that the volcanic gases do not reach equilibrium with surface contaminants such as ground water. A similar comparison of samples collected at the solfataric fumarole Sulphur Bank, which is associated with Kilauea, showed it to be in equilibrium, presumably because mixing with water occurred at greater depths. The presence of increased amounts of sulfur in the form of  $\text{H}_2\text{S}$  was noted in the Sulphur Bank gases prior to and during eruption at Kilauea. This was attributed to increased degassing of the magma, minimizing contamination of the gases. A consideration of the various substances contaminating volcanic gases leads to the conclusion that the primary magmatic gas is more reduced, and contains less  $\text{H}_2\text{O}$  and more sulfur gases than any of the samples collected from the vent-line and pumice heap sites during the eruption.

The staff of the Hawaii Volcano Observatory, U. S. Geological Survey, has developed techniques for drilling through the crust and into the molten core of the lava lakes described above. The drill holes have been used for a variety of researches by the U. S. Geological Survey group, and we have been cooperating in work on the evolved gases.

Early attempts at lava lake gas collection and analysis were made at Kilauea Iki, and the results have been published (1). Sporadic collections were made at the Alae lava lake during the period of its solidification and some of the data is listed in Table I. This work was done while we were restarting gas researches after a two year lay-off, and variations in our collecting equipment and analysis systems were being tried out.

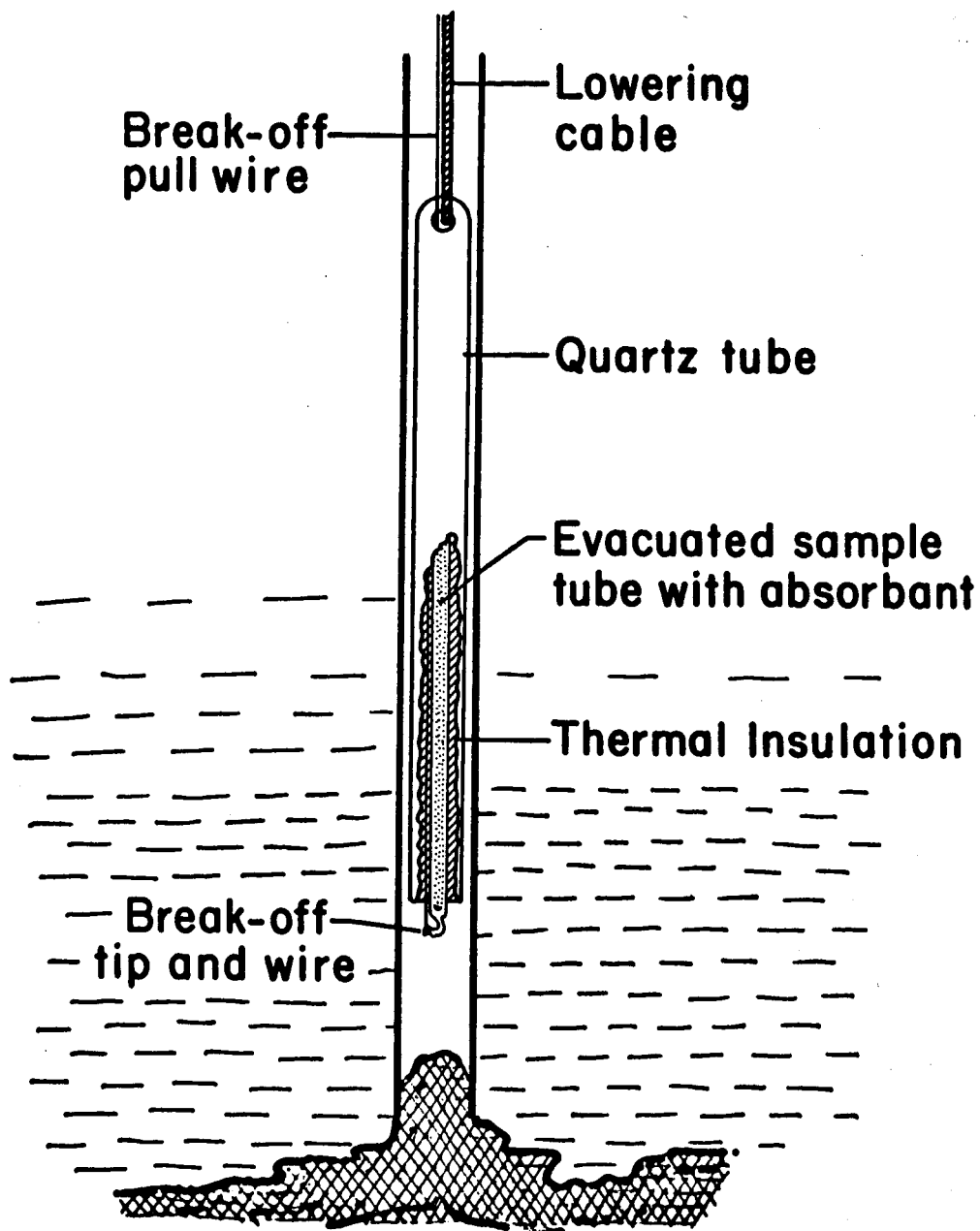
We were fortunate early in March 1965 to have had a flank eruption of Kilauea volcano. This occurred along a rift extending from a prehistoric pit crater (Makaopuhi) to inaccessible regions in the rain forest. It persisted for about two weeks, and in its later phases lava fountaining was limited to a rift on the wall of the pit crater which was filled with molten lava to a depth of approximately two hundred feet. Exact details will be published by the U. S. Geological Survey.

During two periods of the eruption, with the help of the staff of the Hawaii Volcano Observatory, we were able to get a group to the edge of the lava lake under extremely difficult

and unpleasant conditions. Gas samples were taken directly from the surface of the fluid lake and from the momentarily persistent holes left after the removal of ceramic tubes which were used to collect molten lava samples. The U. S. Geological Survey staff has been kind enough to undertake drilling through the crust of the new lake at Makaopuhi at several intervals during the past year to satisfy the needs of gas collection, and samples have been taken both at the bottom and at intermediate levels in these holes. The results of the analyses of samples which have been processed to date are listed in Table I.

Gas collections by adsorption tube techniques have been made as frequently as possible at the old fumarole at Sulfur Bank on the rim of Kilauea Caldera, in order to follow any changes of gas composition with the erupting phase of the volcano. A new solfataric area on the south rim of the caldera, pointed out by Dr. Howard Powers of the Observatory, also has been sampled. Some results are reported (Table I), but analyses have not been completed on these samples as yet due to the press of lava-lake work, and they are stored for the future. Storage does not seem to affect the composition of gases in these tubes.

By the use of enclosed crushers of various designs, gases have been released from some samples of lava and pumice collected within a few days of eruption, and analyzed by means



**Drill Hole Gas Sampling Device**

Fig. 1

of gas chromatography. Satisfactory gas releasing techniques were investigated, and  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{N}_2$  has been found, but no systematic study has been made as yet. Also the gases present in the fluid inclusions in nodules of the 1801 eruption of Hualalei volcano were examined by this same method. These last showed large amounts of  $\text{CO}_2$ , with water and  $\text{N}_2$ . Also large quantities of radiogenic argon-40 were found, which has significance relevant to the potassium-argon dating of volcanics (2).

#### Equipment and Technique Modifications

Gas adsorption tubes utilizing the chromatographic principle, which have been described previously (3) continue to be used for surface collections. Some slight but important modifications have been made in the design of these tubes, but the basic principle and method of use remains the same.

In order to withstand the high temperatures inside drill holes at collection points (to  $1200^\circ\text{C}$ ), adsorption tubes were enclosed in vitreous silica tubes with the intermediate space filled with a diatomaceous earth thermal insulating material. The break-off tip of the tubes could be broken by impact at the bottom, or by a "traveler" or pull-wire at intermediate positions in the drill hole (see Fig. 1). Under ideal conditions these tubes are sealed by the radiant heat from the drill-hole wall, but generally they are withdrawn and sealed directly with a torch. Collection and sealing takes place



in about 2 minutes, and in the period of sealing the sample tube is still being raised in temperature by the heat stored in the outer insulating tube, so the gases exhibit a pressure greater than atmospheric, and "blow-out". This minimizes the tendency to draw in atmospheric gases or combustion gases from the sealing torch.

After the removal of gaseous constituents from the collecting tubes for analysis, the tubes have been used as chromatographic columns and eluted with organic solvents, water and acid. Also condensate water from collection tubes and fumaroles has been extracted into organic solvents, and separate portions were extracted and evaporated to dryness after making neutral, acidic and basic. The derived materials have been examined by qualitative chemical tests and have been pelletized with KBr for analysis using infrared adsorption. Important quantities of ammonium and ferric chlorides, sulfates and phosphates(?) have been found, but these have not been incorporated into our quantitative treatment of data as yet.

The main method used for gas analysis was the important technique of gas chromatography. The particular combination of major component gases found in volcanic effluvia is difficult to analyze accurately by any method, and we are continually changing our equipment in order to simplify and improve this technique. The trend is to use a single detector with multi-column switching to accommodate the variety of components to be

analyzed. In order to detect carbon containing molecules which might be present in very minor amounts in the gases, a flame ionization detector system has been installed.

Attempts have been made to use a small quartz spectrograph for analysis of the drill hole gases in situ by absorption spectrometry. The hot lava at the base of the hole then serves as a continuum source, and the drill hole is the absorption cell with its sample of hot gas. The technique is illustrated in Figure 2, which is self explanatory. The results from one of the first attempts to perform this experiment are shown in Figure 3, and it can be seen that a great many molecular band systems are in evidence to which some very tentative assignments have been made. It is evident that this technique will bear much further investigation, with possible applications even at erupting vents. The wealth of information regarding high temperature naturally occurring gas components that may come with improvements in the technique and better equipment is obvious. We are attempting some phases of this work.

#### Discussion of Results

As noted, results for the volcanic gas analyses which have been made to date are given in Table I. The location of the drill holes in Makaopuhi Lava lake, the principal lake studied, are shown mapped in Figure 3a. Examination of the

# Lava Lake Absorption Spectroscopy

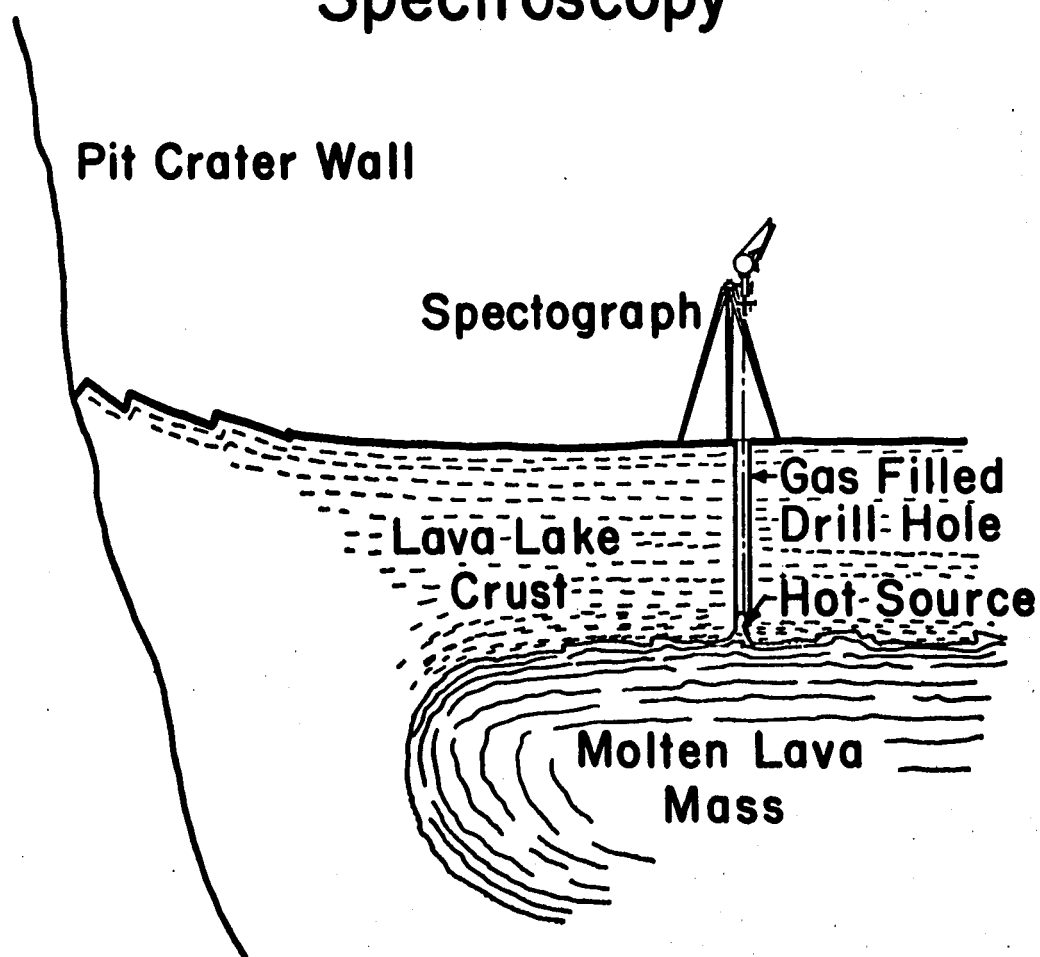


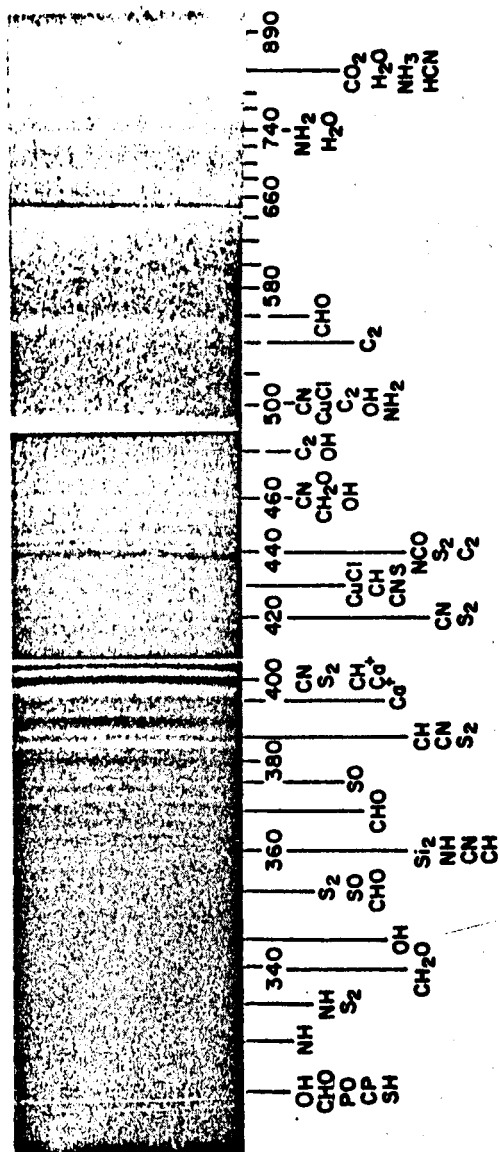
Fig. 2

# ABSORPTION SPECTRUM

Makaopuhi Lava Lake Drill Hole

No. 21

Nov. 29, 1965



Possible Band Assignments

Fig. 3

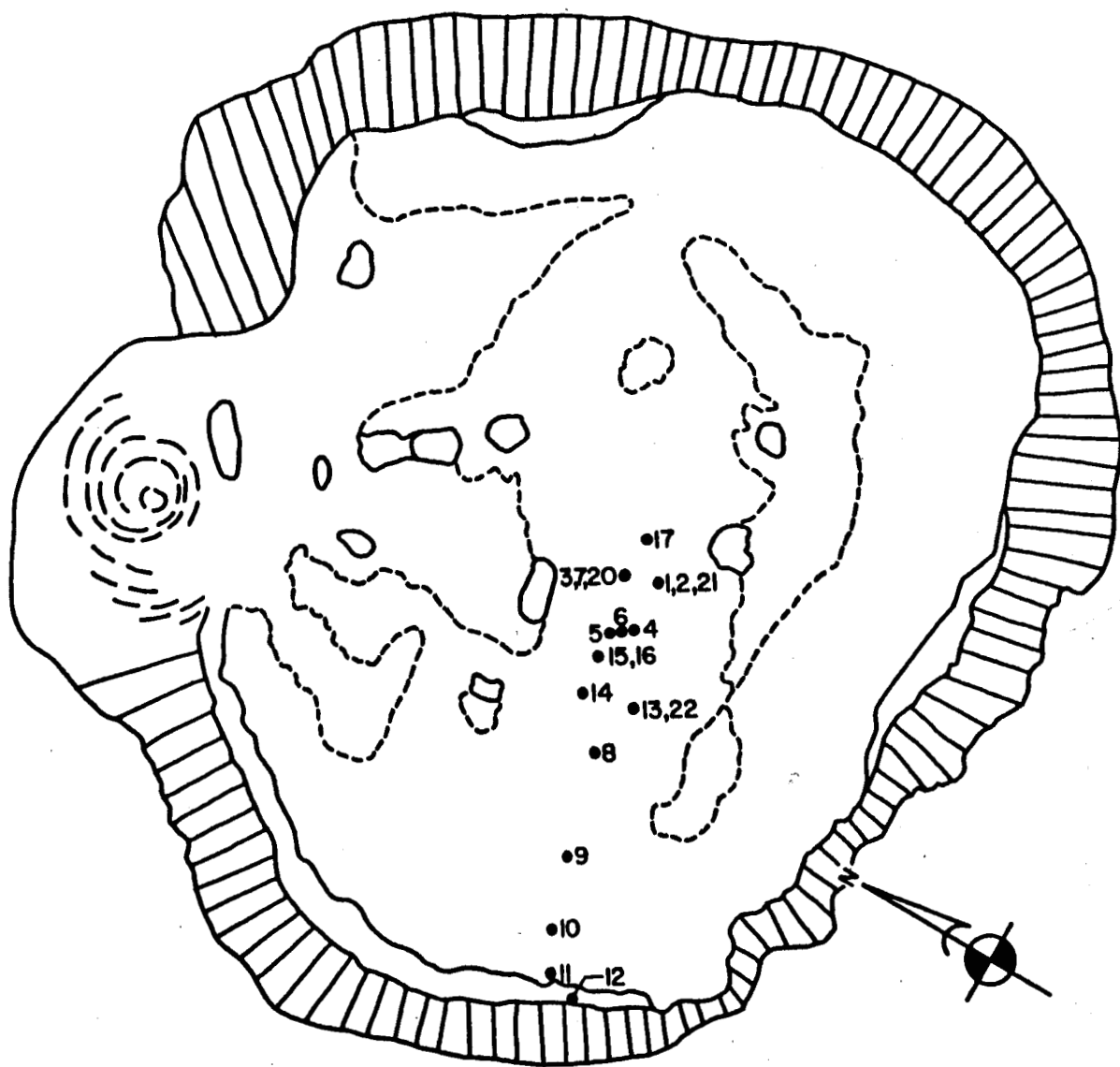


Fig. 3a

results given in the figures and tables demonstrates certain trends and variations which bear examination.

Oxygen content of analyzed gases. Save for some samples collected at a piped fumarole (Sulfur Bank), oxygen and the accompanying nitrogen from air, seem always to be found as measurable components in the gases collected under field conditions. Sometimes there is evident and expected air contamination, as in the gases taken at the surface of the lava lake. At other times even when collection and closure conditions are ideal, with "blow-out" of the gases during sealing, there is found a small content of these gases. Thermodynamically, if equilibrium were to be attained in the gaseous mixture, there should be no measurable reducing gases ( $H_2$ ,  $CH_4$  and  $CO$ ) under such conditions with oxygen present. If air permeation through the lava lake crust extends all the way to the high temperature zone near the bottom of the hole, one would expect in time some approach to equilibrium with a very low content of these reduced gases, since the equilibrium constants for the oxidations are large. The equilibrium concentration of oxygen extends from about  $10^{-8}$  mole per cent at  $1200^\circ C$  to even lower values at lower temperatures.

The other possibility is that our "ideal" collecting procedures still allow some contamination by air. How this happens is not understood as yet, but all possible sources are being examined. Changes in tube design and in operating

procedures are being undertaken to try to remedy this defect. Certainly the contained oxygen does not seem to react appreciably, so the procedure of correcting for air to the "air free" basis, as is shown in the tables of data, is valid as an interim procedure at this stage.

Variation of Gaseous Composition. Since, as has been explained, the volcanic gases represent a system in homogeneous equilibrium, a compositional variation with depth in the drill holes is to be expected as a consequence of the temperature gradient. The equilibrium component variation with temperature for a gas of bottom composition is shown in Figure 4. This has been machine plotted from computer data calculated by the method of minimizing the free energy of the system. In general, the major components tend to vary in the mode predicted (note particularly the oxygen partial pressure) save in the upper reaches of the drill holes. There is indication that surface waters penetrate to some extent through the rock crust, and thus account for the observed higher water content of gases collected in the upper sections (Table I). That there should be an indication of penetration is of great interest in connection with the whole question of contamination of volcanic hot zones by fluids penetrating from the surface. Evidently there is sufficient flow gradient of gases from the cooling lava body to act to some degree to prevent or inhibit penetration.

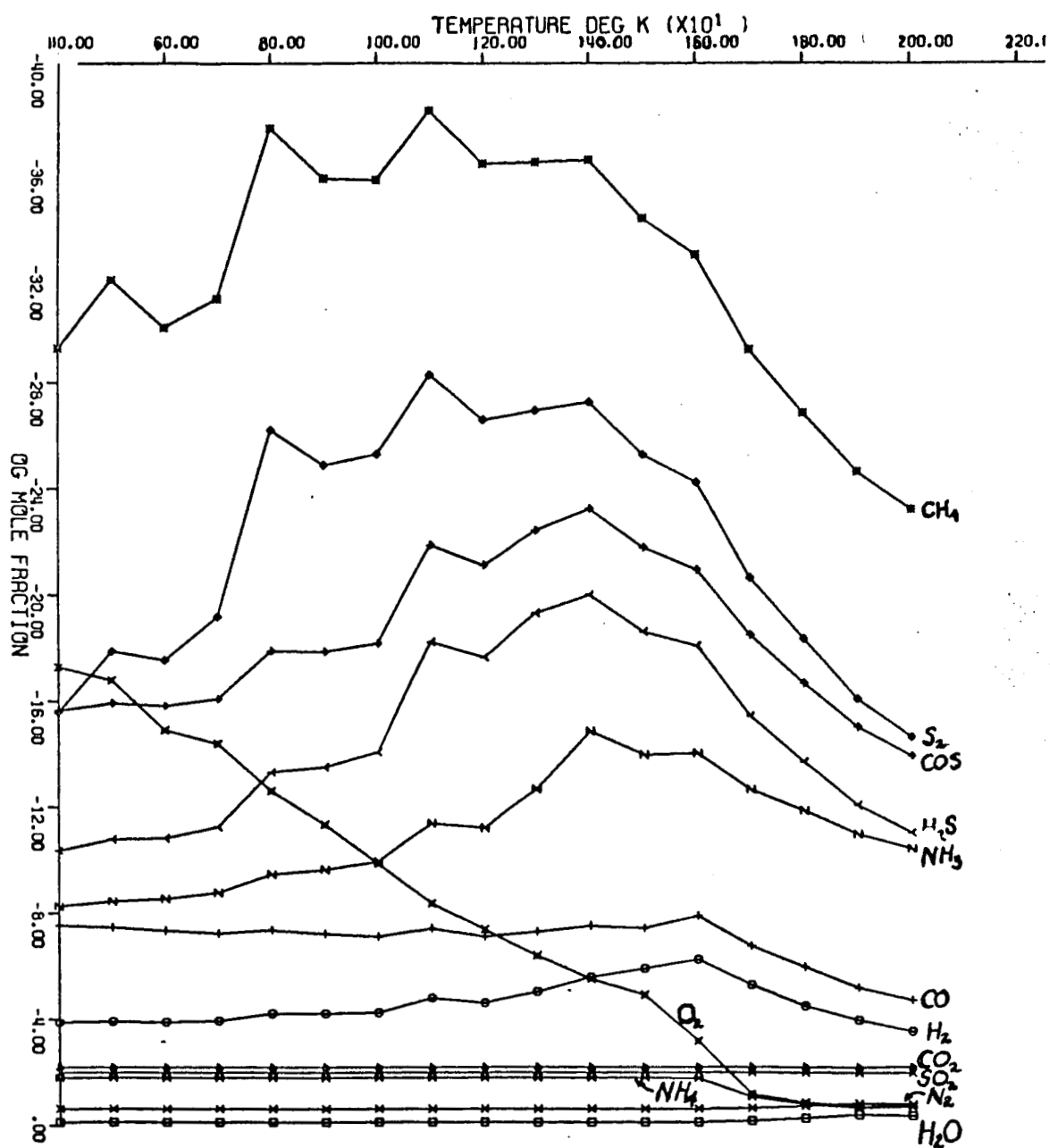


FIG. 4



This in turn may be related to a greater degree of permeability of the upper cooler levels due to fractures caused by contraction cooling, while the hotter zones may still be in a less-open expanded condition.. It will be interesting to note how this depth of water penetration proceeds with continued cooling of the lava lakes. On the larger question of the contamination of a static magma body by surface fluids--for example, the primary magma chamber beneath a volcano, one would expect the same conditions to hold--that penetration would be limited by out-flowing volatiles and lesser permeability.

It is noteworthy that the composition of the gases seems to vary from one drill hole to another at a given time. This is also to be noticed for the sulfur gases at cracks on the lake surface, certain of which will emit a high concentration of sulfur gases, and others not. To explain this phenomenon, one may have resort to the existence of large convective cells or pods in the liquid magma beneath. Such slow flowing action would serve to concentrate volatiles in regions of upwelling, and give the observed uneven distribution. Up to now, there is no definite experimental evidence for such a convective cell mechanism. For certain locations such as those near the edge of the lava lake (drill hole No. 12) compositional variations would be expected. Here solidification would have progressed further in the section of the lake feeding gases

to the hole, the temperature profile would be different, and surface gas infiltration would be more important. Analyses of gases from such holes reflect this last factor very strongly.

Trends. Many of the gas collections which have been made have been faulty due to very evident accidents or poor collecting situations (breakage, poor sealing of tubes, micro leaks, unbearable collection environment, etc.). As noted above, for other samples the reasons for the poor collections are not evident. Since a considerable effort and expenditure go into expeditions to the volcano area, collections are made sporadically, and progress is slow in developing improved methods of field sampling. The most fool-proof technique as developed and tested in the laboratory seldom works as expected in the field. Lacking at present the ideal gas collection and analysis instruments, we are obliged to discard many of our collections as being unsatisfactory, or make some adjustment when they do not adhere to some set standard, which has been arbitrarily set up at present. The correction to the "air free" condition discussed above is one such adjustment. Also a criterion of satisfactory sampling based on the level of contamination can be justified. It is evident that samples even from a good collecting situation such as the bottom of a drill hole, which contains 90% air or 99% water, are defective. Accordingly we have discarded samples with approximately 10% or more air content in discussing trends.

These trends may be noted, as follows:

1. The thermodynamic variation of oxidized to reduced species which is found as one goes from cold to hot areas--say, from lava lake surface to drill hole, or from top to bottom in a drill hole. These are noted mainly in the oxygen partial pressure variations, and have been mentioned previously.

2. A large decrease in the carbon dioxide content from the active lava immediately after eruption, to the lava lake, when the content becomes minor and constant at approximately 0.03% (air free).

3. A possible decrease in the free nitrogen content during the history of the cooling of the lake.

4. The appearance of methane in small amounts in the later history of the lava lake. This would seem to preclude a contribution from pyrolyzing vegetation as an important component of the gases. Collections made from lava flows covering vegetation always show a large content of methane, and this is predominant in the early phases of cooling of these flows.

5. A trend in the sulfur gases which to some degree, parallels the behavior of carbon dioxide--a large content in newly erupted lava, decreasing to minor amounts in the cooling lava lake. This gas is usually  $\text{SO}_2$  (approx. 0.2%), with  $\text{H}_2\text{S}$  appearing on occasion. Sulfur gases are difficult to preserve unreacted during collection and analysis. Calcium sulfate

appears as an important component among condensed volatiles, which is difficult to reconcile with the known volatilities of inorganic compounds. It can be said that the sulfur chemistry of volcanic systems is still very poorly understood.

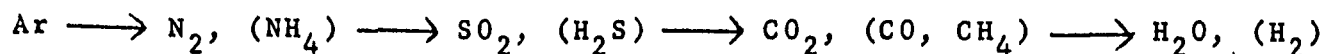
In the light of the above, the analysis of gases collected at Sulfur Bank fumarole would appear to be of interest. These gases come from a relatively cool fumarole (approx. 95°C), and probably contain much meteoric water. From previous calculations they have been shown to represent an equilibrium system (1). The air free collections which are possible with the technique used at this site are interesting. In addition, high contents of carbon dioxide and sulfur gases point to a direct connection between this outlet and a primary lava body. From previous studies which are still in progress, these gases have been shown to present an interesting variation in the sulfur gas content, and in the ratio of oxidized to reduced species in the sulfur gas ( $\text{SO}_2/\text{H}_2\text{S}$ ) with the phase of activity in nearby Kilauea volcano.

Absorption Spectra. The absorption spectrum of the drill hole gases reveals a wealth of species producing band systems that merit further study. Beyond the very tentative assignment of some molecules and free radicals to these bands (Figure 3), little further can be said at present. Before definite assignments can be made, further study in the laboratory and in the field must be undertaken using improved equipment.

Preparations are now being made to carry on this work.

General Conclusions - Collecting Sites and Nature of  
Major Components.

It would appear from the results of the analyses of volcanic and lava lake gases which have been made to date, that we are dealing with somewhat different situations as far as volatiles are concerned when we compare gas from the lava lake with that from the primary volcano. In either system water is of primary importance and is the connecting link between them. It probably is the most soluble of the major gases in magma at high temperatures and, at both high and low pressures. Doubtlessly in any "reaction series" showing the sequence of separation of the volatiles from a fluid magma with temperature and pressure decrease, it would be the last substance to separate. One may make a hypothetical, and tentative, reaction or gas evolution series of this type based on observed lava lake trends, fumarolic gases, and gases found in inclusions from deep-seated sources, as follows:



The major reduced species associated with each gas, under the appropriate thermodynamic conditions, is indicated parenthetically. The amounts of volatiles separating would be in

quite the reverse order, with water the major component and the others decreasing in quantity to a minor content of argon. Some equilibrium concentration of each would be present at all stages.

General Conclusions - Biological Precursors in Volcanic Gases.

The general model of a prebiotic molecular environment which has grown from the work of Calvin, Miller, Fox, Oro, Ponnampersuma and others, is one made up of water, carbon dioxide, methane, ammonia and hydrogen. This is just the atmosphere which would be provided by the volatiles evolved in volcanism, and, in the main, would require adjustments only in the relative quantities of the molecules to conform to the primeval atmospheres assumed by these workers.

The oceanic Hawaiian volcanoes are believed to represent a primitive system with a minimum of reworked crustal material present in eruption products, because of the non-orogenic nature of the crust in the region. The volatile products are found in combination to give a rather acidic medium (see Table I), and until recently have not been seriously examined for basic ammonia. As has been emphasized, the gaseous system is an equilibrium one, and when thermodynamic data for the acidic gaseous form  $\text{NH}_4$  was found and used in equilibrium calculations, this was shown to be a potentially important component

(Figure 4). Once condensed in collecting tubes this is not re-evolved easily as a gas, and was not detected until we included in our procedures a chromatographic elution step to remove non-gaseous materials, as has been explained. We have, then, the complete list of molecules in Hawaiian volatiles which are needed to give a primitive atmosphere with biotic potential. From these studies a tentative rough composition could be given, and it would be as shown in Table II.

TABLE II

Approximate Composition of a Primitive Atmospheric-Aqueous System Based on Hawaiian Volcanic Volatile.

		Composition (Mole %)
H <sub>2</sub> O	-	66
H <sub>2</sub>	-	1
CO <sub>2</sub>	-	18
CH <sub>4</sub>	-	10 <sup>-4</sup>
SO <sub>2</sub>	-	10
H <sub>2</sub> S	-	10 <sup>-4</sup>
N <sub>2</sub>	-	5
NH <sub>4</sub>	-	10 <sup>-2</sup>

Sulfur gases, which would be needed at some stage in biogenetic development, are reactive towards rock components and would be incorporated in these and disappear from the

volatile environment. This has been noted in the analysis of the volatiles in volcanic rock vesicles and gaseous inclusion, when sulfur volatiles are not usually found.

There remains, then, to supply the energy needed for the conversion of some part of the components of the volatile system to molecules which are more closely associated with biotic systems--amino acids, simple organics, nucleic acid constituents and proteinoids. In the laboratory electric discharges, ultra-violet light and ionizing radiation have been used, and Fox has found that heat alone will suffice. Certainly there is an abundance of heat as an energy source in volcanic systems.

In addition to the irreversible processes which might be induced by transient exposure to the above-mentioned sources of energy, it has been shown (3) that the maintenance of thermodynamic equilibrium in mixtures of primeval composition will suffice to produce a variety of simple carbon containing compounds which could play an important role in the chemical evolution of biological substances. A method of looking at such a thermodynamic system as a three component system of O, C and N is shown in Figure 5. The position of volcanic volatiles in the system is shown by the black square points; "1" representing the volcanic gas with an amount of nitrogen equal to carbon assumed, and "2" showing the same system with some of the oxygen removed as sulfur compounds. It can be seen that point



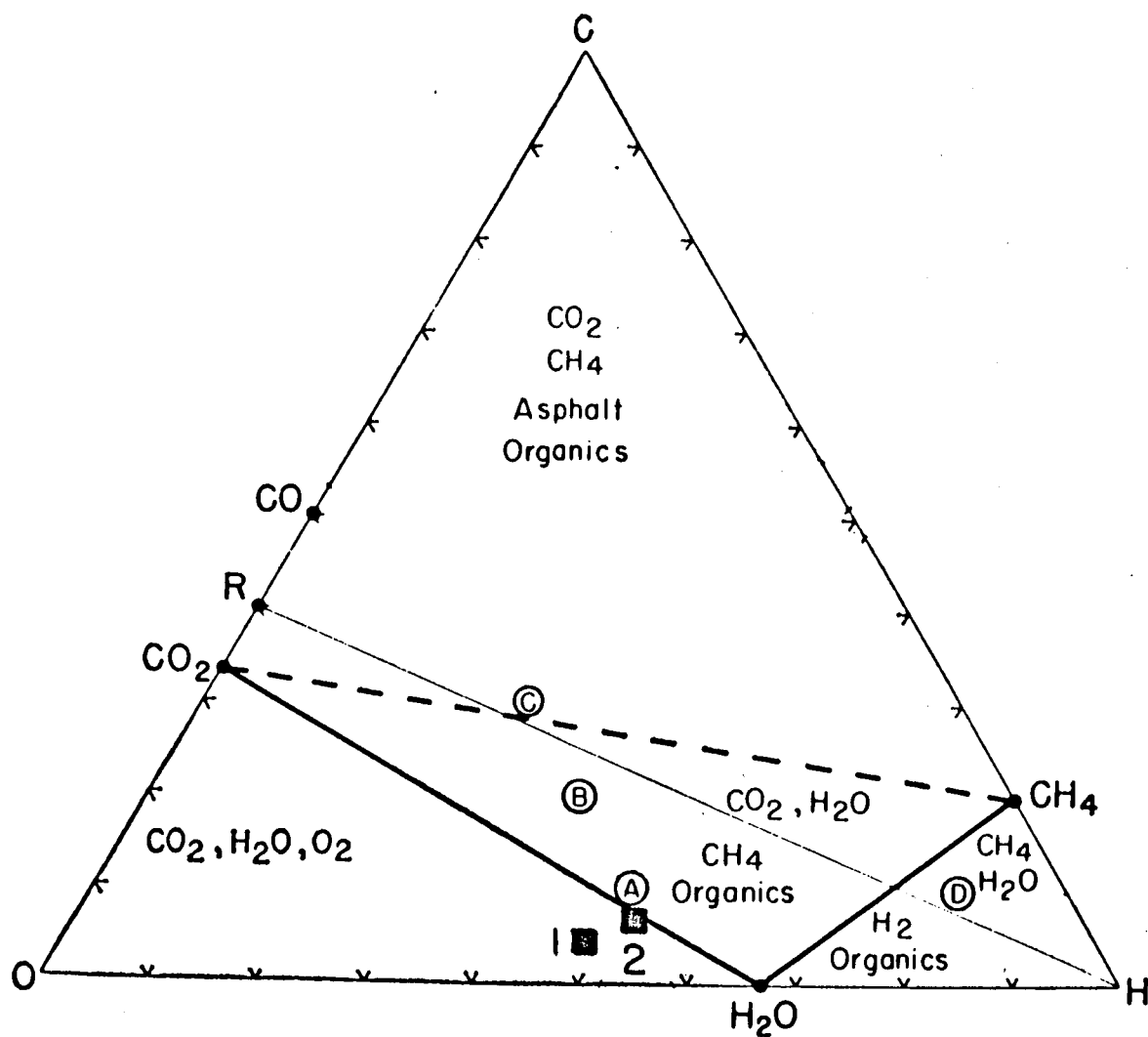


Fig. 5

"2" approaches the region where methane and organics become important. Of the latter, nitriles, amines and various aldehydes would be of chief interest from the prebiotic viewpoint.

It may be concluded that either non-reversible conversion of atmospheric-aqueous systems of volcanic volatile composition by high energies supplied by transient sources, or thermodynamic equilibrium achieved in these systems, would act to produce molecules which would be important in the chemical stages of evolution towards biological molecules. It remains to detect some of the molecules representing intermediate steps in these processes. Thus far our detectors have not been able to pick up such in the gases. It is hoped that with the use of newly developed flame detectors sensitive to phosphorus compounds, and halogens (which, in the same sense as with ammonium compounds, we are finding as important gaseous components), some evidence of these will be found. Also our "flow-through" mass spectrometer, which is finally just going into successful operation, will soon be used in the search for these important substances.

#### Personnel

Currently the work is proceeding with the use of student help and one graduate research assistant (Bruce Finlayson). We are in the process of seeking a candidate to fill the post-doctorate position, which will be done in the next month or so with some excellent prospects at hand.

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TABLE I

## GAS SAMPLE ANALYSES

## Drill Holes, Lava Lake and Sulfur Bank Fumarole

## Concentrations, Mole Per Cent

Sample	Depth Ft.	H <sub>2</sub> O	H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	CO	SO <sub>2</sub>	H <sub>2</sub> S	CH <sub>4</sub>	Comment
Sulfur Bank Fumarole, 7/2/64.	--	94.9 95.2	-- --	0.30 --	1.5 0.41	3.3 3.3	-- --	-- --	0.006 0.006	-- --	(1.4% air) Air free.
Sulfur Bank Fumarole, 2/3/65.	--	91.9 92.3	-- --	0.08 --	0.59 0.29	7.4 7.4	0.0001 0.0001	-- --	-- --	-- --	(0.38% air) Air free.
Sulfur Bank Fumarole, 6/17/65.	--	94.3 94.3	5.53x10 <sup>-4</sup> 5.53x10 <sup>-4</sup>	-- --	0.0128 0.0128	5.75 5.75	-- --	0.137 0.137	0.00684 0.00684	-- --	No air. Air free, 96°C.
Sulfur Bank Fumarole, 7/19/65.	--	87.6 89.46	0.00328 0.003	0.554 --	1.70 (-0.37)	9.96 10.17	0.0160 0.016	0.347 0.354	-- --	-- --	(2.63% air) Air free, 96°C.
Drill Hole 9, Alae, 2/2/65.	48	11.5 67.0	tr. --	17.4 --	70.6 31.0	0.52 3.2	0.008 0.05	-- --	-- --	-- --	(83% air) Air free.
Makaopuhi Lava Lake, 3/7/65. "Hole" in lava lake.	0	4.0 33.0	-- --	18.5 --	76.5 50.7	0.51 4.2	-- --	1.4 12.0	-- --	-- --	(88% air) High air contamination. Air free.
Surface Makaopuhi Lake, 3/7/65.	0	9.44 98.03	0.00548 .057	20.4 --	75.3 (-73)	0.184 1.91	-- --	-- --	-- --	-- --	(96.43% air) Air free.
Surface Makaopuhi Lake, 3/7/65.	0	4.95 97.52	0.0575 1.13	21.2 --	77.6 (-1.41)	0.0981 1.34	-- --	-- --	-- --	-- --	(100% air) Air free.
Drill Hole 6, Makaopuhi, 6/18/65.	9	22.3 22.7	-- --	0.3 --	64.4 64.3	4.8 4.9	-- --	8.0 8.1	-- --	-- --	(1.4% air) Air free, 1150°C.

TABLE I - continued

Sample	Depth Ft.	H <sub>2</sub> O	H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	CO	SO <sub>2</sub>	H <sub>2</sub> S	CH <sub>4</sub>	Comment
Drill Hole 12, Makaopuhi, 6/18/65.	20	93.9 99.5	-- --	1.2 --	4.8 0.32	0.14 0.15	0.006 0.006	0.02 0.02	-- --	-- --	(5.7% air) Air free, 680°C.
Drill Hole 9, Makaopuhi, 6/18/65.	9	96.9 99.45	-- --	0.757 --	2.75 --	0.021 0.020	-- --	-- --	0.0235 0.023	-- --	(3.56% air) Air free, 1000°C.
Drill Hole 11, Makaopuhi, 7/20/65.	5	28.2 95.14	-- --	13.9 --	53.2 4.71	0.0658 0.16	-- --	-- --	-- --	-- --	(65.7% air) Air free, 490°C.
Drill Hole 11, Makaopuhi, 7/20/65.	7	29.5 97.22	0.199 0.66	15.0 --	56.4 1.63	0.446 0.49	-- --	-- --	-- --	-- --	(70.9% air) Air free, 650°C.
Drill Hole 11, Makaopuhi, 7/20/65.	5	26.4 66.20	-- --	10.9 --	54.0 33.65	0.0734 0.15	-- --	-- --	-- --	-- --	(51.5% air) Air free, 490°C.
Drill Hole 11, Makaopuhi, 7/20/65.	7	33.7 60.30	-- --	9.13 --	56.4 39.54	0.0916 0.16	-- --	-- --	-- --	-- --	(42.4% air) Air free, 650°C.
Drill Hole 8, Makaopuhi, 7/21/65.	4	98.1 98.29	0.0115 .011	0.0350 --	1.48 1.35	0.0288 0.03	-- --	0.346 0.35	-- --	-- --	Raining; sulfur hole. (0.14% air) Air free, 500°C.
Drill Hole 8, Makaopuhi, 7/21/65.	9.6	90.8 98.78	0.174 0.19	1.51 --	6.54 0.99	0.0320 0.03	-- --	-- --	-- --	0.0019 0.002	Raining (7.14% air) Air free, 900°C.
Drill Hole 14, Makaopuhi, 7/21/65.	5	94.0 95.06	0.0354 0.035	0.276 --	5.73 4.75	0.0332 0.033	-- --	0.109 0.110	-- --	5x10 <sup>-4</sup> 5x10 <sup>-4</sup>	(1.30% air) Air free, 540°C.
Drill Hole 14, Makaopuhi, 7/21/65.	8.6	77.1 82.10	0.837 0.89	0.705 --	18.5 16.90	0.0866 0.091	-- --	-- --	-- --	0.0212 0.021	(3.33% air) Air free, 820°C.
Drill Hole 14, Makaopuhi, 7/21/65.	11	62.0 72.83	2.11 2.48	2.44 --	29.0 23.39	0.481 0.56	-- --	0.614 0.72	-- --	0.0163 0.019	(11.5% air) Air free, 960°C.

TABLE I - continued

Sample	Depth Ft.	H <sub>2</sub> O	H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	CO	SO <sub>2</sub>	H <sub>2</sub> S	CH <sub>4</sub>	Comment
Drill Hole 16, Makaopuhi, 7/21/65.	7	11.2	0.0031	20.6	69.8	0.151	--	--	--	+	(97.4% air)
		98.90	0.027	--	(-6.98)	1.08	--	--	--	--	Air free, 720°C.
Drill Hole 16, Makaopuhi, 7/21/65.	12	63.1	1.19	2.01	33.2	0.134	--	--	--	0.0348	(9.50% air)
		62.99	1.19	--	25.71	0.131	--	--	--	0.034	Air free, 980°C.
Drill Hole 11, Makaopuhi, 11/27/65.	7	97.4	0.0448	0.351	1.71	0.0271	--	0.259	--	--	(1.65% air)
		99.27	0.045	--	0.42	0.027	--	0.259	--	--	Air free, 500°C.
Drill Hole 11, Makaopuhi, 11/27/65.	6	98.5	0.0074	0.326	1.26	0.0098	--	--	--	--	(1.54% air)
		99.94	0.007	--	0.04	0.0098	--	--	--	--	Air free, 420°C.
Drill Hole 20, Makaopuhi, 11/29/65.	14.5	96.7	0.179	0.577	2.61	0.216	--	--	--	5.77x10 <sup>-4</sup>	(2.75% air)
		99.12	0.183	--	0.47	0.22	--	--	--	5.8x10 <sup>-4</sup>	Air free, 900°C.
Drill Hole 20, Makaopuhi, 1/31/66.	3	98.2	0.0774	0.0877	1.68	0.0651	--	--	--	7.29x10 <sup>-5</sup>	(0.41% air)
		98.58	0.077	--	1.27	0.065	--	--	--	7.3x10 <sup>-5</sup>	Air free, 270°C.
Drill Hole 20, Makaopuhi, 1/31/66.	7	98.0	0.0497	0.296	1.90	0.0285	--	--	--	--	(1.40% air)
		99.11	0.050	--	.81	0.029	--	--	--	--	Air free, 500°C.
Drill Hole 20, Makaopuhi, 1/31/66.	10	96.3	0.0400	0.675	2.98	0.00834	--	--	--	2.67x10 <sup>-4</sup>	(3.19% air)
		99.47	0.040	--	0.48	0.008	--	--	--	2.7x10 <sup>-4</sup>	Air free, 700°C.